

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-109620

(43)Date of publication of application : 23.04.1999

(51)Int.Cl.

G03F 7/022
C08G 69/32
C08K 5/13
C08K 5/23
C08L 77/06
G03F 7/037
G03F 7/075
H01L 21/027

(21)Application number : 10-217692

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(22)Date of filing : 31.07.1998

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HIRANO TAKASHI

(30)Priority

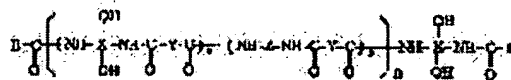
Priority number : 09214243 Priority date : 08.08.1997 Priority country : JP

(54) POSITIVE PHOTSENSITIVE RESIN COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a photosensitive resin compsn. having high sensitivity, capable of obtaining a pattern with a high rate of a residual film and excellent in adhesion to a sealing resin by composing the resin of specified polyamide, a photosensitive diazoquinone compd. and a specified phenol compd.

SOLUTION: A photosensitive resin comopsn. consists of 100 pts.wt. polyamide represented by formula I, 1-100 pts.wt. a photosensitive diazoquinone compd. and 1-30 pts.wt. a phenol compd. represented by formula II. In the formula I, X is a tetravalent cyclic compd. group, Y is a divalent cyclic compd. group, Z is-R1Si(R3)(R4)-O-Si



I



II

(R3)(R4)-R2- (each of R1 and R2 is a divalent org. group and each of R3 and R4 is a monovalent org. group) E is an alkenyl group or an aliphatic or a cyclic compd. group having the alkenyl group, each of a, b is a molar fraction, $a+b=100$ mol.%, (a) is 60.0-100.0 mol.%, (b) is 0-40.0 mol.% and (n) is 2-500. In the formula II, R5 and R6 are each an H atom or a alkyl group and R7-R10 are each an H atom, a halogen atom, an alkyl group or the like.

LEGAL STATUS

[Date of request for examination] 18.05.2001

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number] 3449925

[Date of registration] 11.07.2003

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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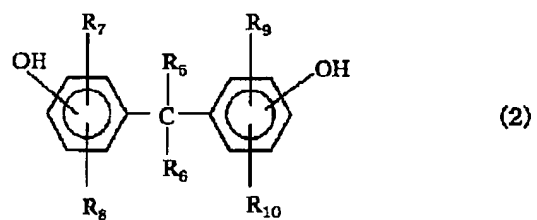
JAPANESE

[JP,11-109620,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE
INVENTION TECHNICAL PROBLEM MEANS EXAMPLE

[Translation done.]

Drawing selection Representative drawing



(式中、 R_5 , R_6 は水素原子またはアルキル基を表し、

R_7 , R_8 , R_9 , R_{10} はそれぞれ水素原子、ハロゲン原子、水酸基、

アルキル基、アルコキシ基、シクロアルキル基の内から選ばれ

た1つを示す)

[Translation done.]

* NOTICES *

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1. This document has been translated by computer. So the translation may not reflect the original precisely.

2. **** shows the word which can not be translated.

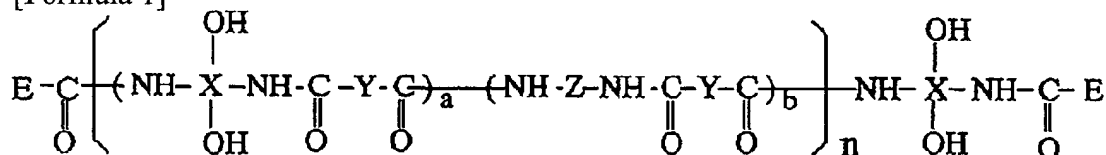
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

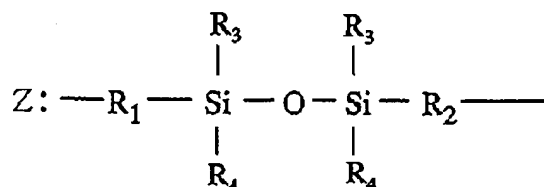
[Claim 1] a general formula -- (-- one --) -- being shown -- having -- a polyamide -- (-- A --) -- 100 -- weight -- the section -- photosensitivity -- diazo one -- a quinone -- a compound -- (-- B --) -- one - 100 - weight -- the section -- a general formula -- (-- two --) -- expressing -- having -- a phenolic compound - (-- C --) -- one - 30 -- weight -- the section -- from -- becoming -- things -- the feature -- ** -- carrying out -- a positive type -- a photopolymer -- a constituent .

[Formula 1]



式中 X:4価の環式化合物基
Y:2価の環式化合物基

(1)



(R₁、R₂:2価の有機基、R₃、R₄:1価の有機基)

E:アルケニル基又はアルキニル基を少なくとも1個を有する
脂肪族又は環式化合物基

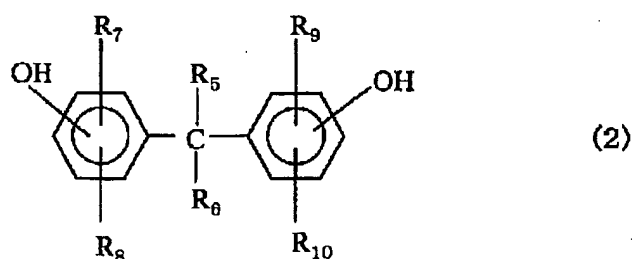
a、b はモル分率を示し、a+b=100モル%

a=60.0~100.0モル%

b=0~40.0モル%

n=2~500

[Formula 2]



(式中、 R_5 、 R_6 は水素原子またはアルキル基を表し、

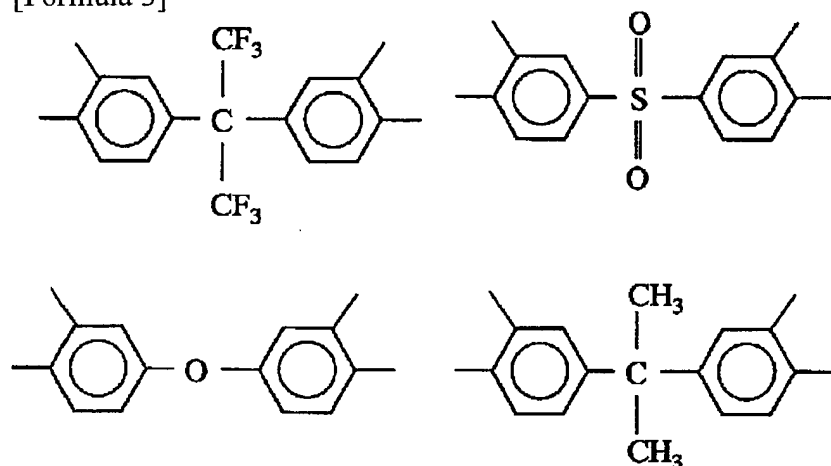
R_7 、 R_8 、 R_9 、 R_{10} はそれぞれ水素原子、ハロゲン原子、水酸基、

アルキル基、アルコキシ基、シクロアルキル基の中から選ばれ

た1つを示す)

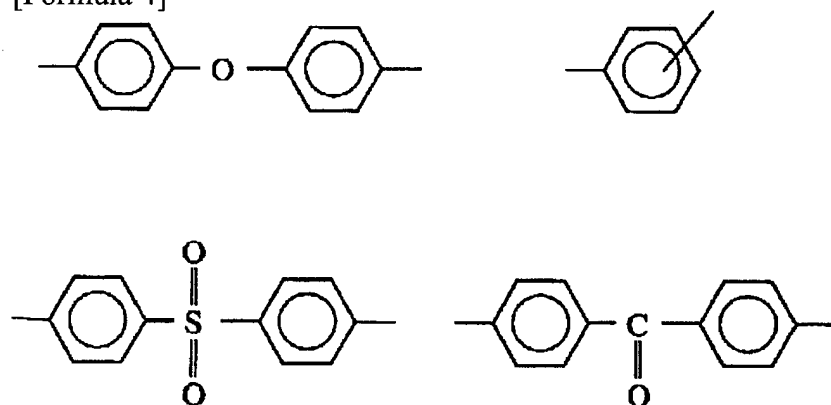
[Claim 2] A positive type photopolymer constituent according to claim 1 with which it comes to choose X in a polyamide of a general formula (1) out of the following.

[Formula 3]



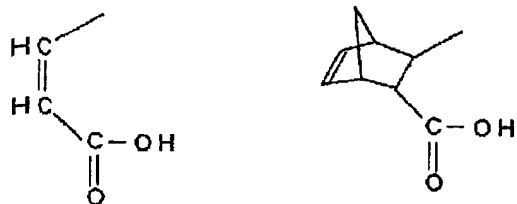
[Claim 3] A positive type photopolymer constituent according to claim 1 or 2 with which it comes to choose Y in a polyamide of a general formula (1) out of the following.

[Formula 4]



[Claim 4] A positive type photopolymer constituent according to claim 1, 2, or 3 with which it comes to choose E in a polyamide of a general formula (1) out of the following.

[Formula 5]

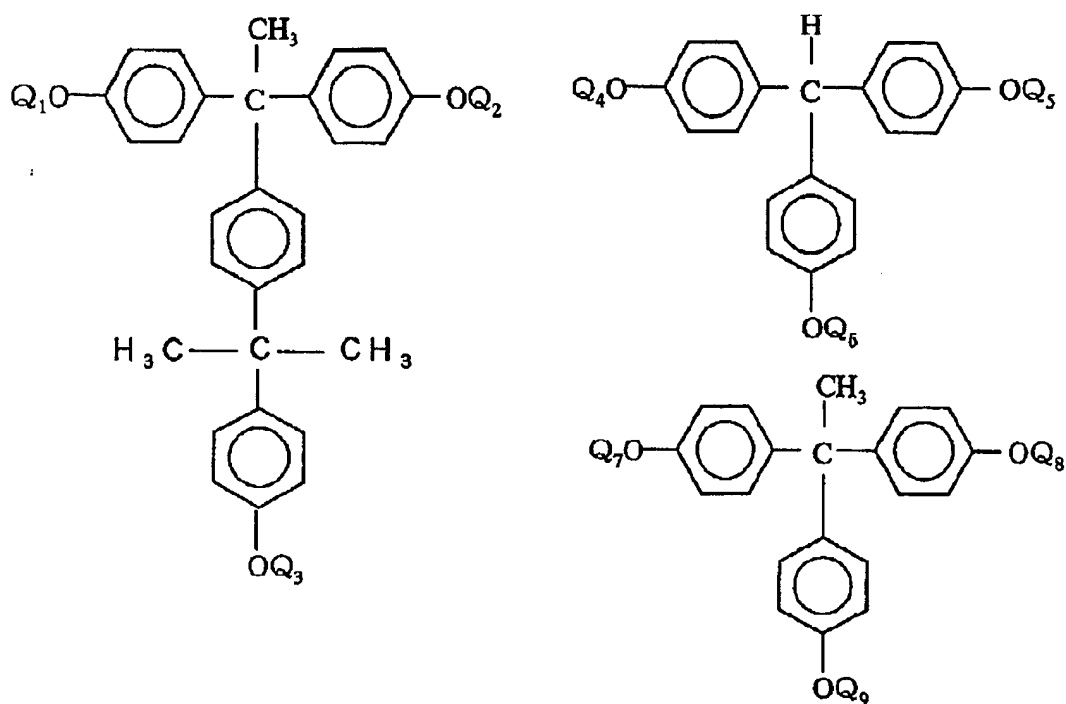


[Claim 5] A positive type photopolymer constituent according to claim 1, 2, 3, or 4 characterized by a polyamide shown by general formula (1) being the mixture of a polyamide (a) weight average molecular weight 5000-17000 and whose molecular weight distribution searched for by Mw/Mn are 1-2, and a polyamide which are (b) weight average molecular weight 30000-70000 and molecular weight distributions 2-4.

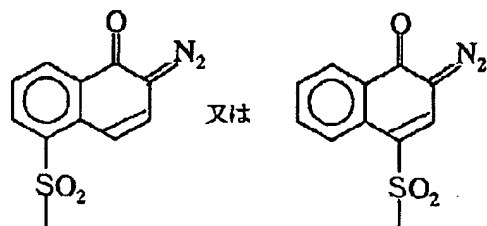
[Claim 6] A positive type photopolymer constituent according to claim 5 with which a (a) component which is a low molecular weight constituent is characterized by containing the whole 20 to 70% of the weight in a polyamide component shown by general formula (1).

[Claim 7] A positive type photopolymer constituent according to claim 1 with which it comes to choose a photosensitive diazo quinone compound (B) out of the following.

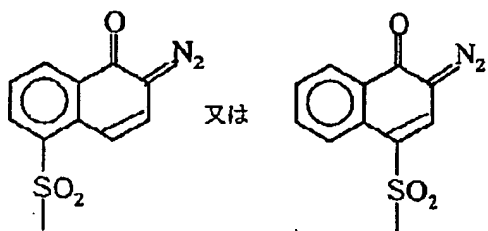
[Formula 6]



(式中 Q_1 、 Q_2 、 Q_3 、 Q_4 、 Q_5 、 Q_6 、 Q_7 、 Q_8 、 Q_9 は水素原子又は



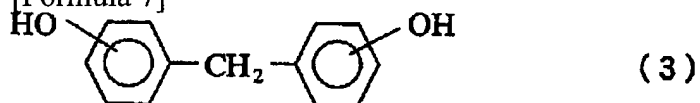
を意味し、 Q_1 、 Q_2 、 Q_3 、 Q_4 、 Q_5 、 Q_6 、 Q_7 、 Q_8 、 Q_9 の少なくとも1つは、



を意味する。)

[Claim 8] A positive type photopolymer constituent according to claim 1 whose phenolic compound (C) is a phenolic compound expressed with a general formula (3).

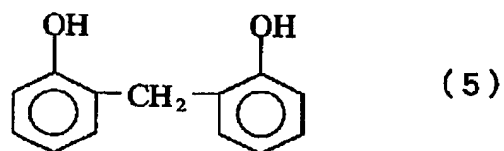
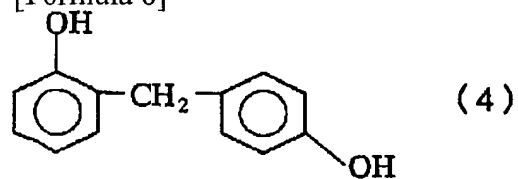
[Formula 7]



[Claim 9] A positive type photopolymer constituent according to claim 1 or 8 with which a phenolic compound (C) is a compound expressed with a general formula (4) or (5), and contains 50% of the

weight or more of the whole phenolic compound (C) in a form of independent or mixture.

[Formula 8]



[Translation done.]

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3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

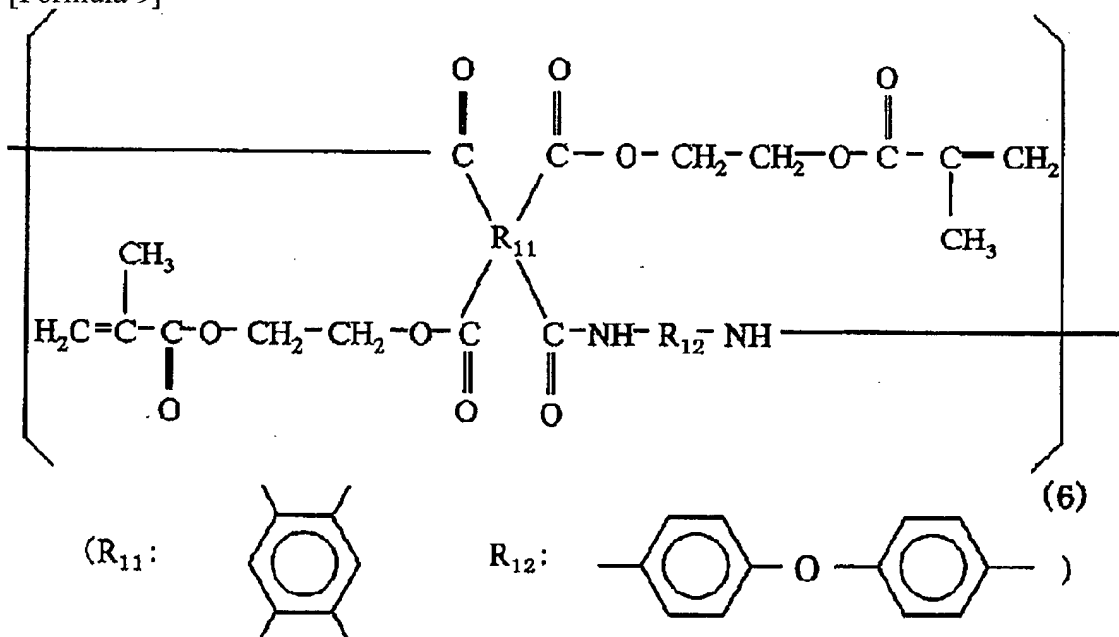
[The technical field to which invention belongs] This invention relates to the positive type photopolymer constituent which could obtain the pattern of a high remaining rate of membrane by high sensitivity, and was excellent in adhesion with closure resin.

[0002]

[Description of the Prior Art] Although the polyimide resin which has the electrical property in which thermal resistance was excellent in and excelled, a mechanical characteristic, etc. is conventionally used for the surface-protection film of a semiconductor device, and the interlayer insulation film, there is a demand of the remarkable improvement in heat-resistant cycle nature, heat-resistant shock nature, etc. in recent years by the shift to the surface mount by high integration of a semiconductor device, enlargement, thin-shape-izing of a package, a miniaturization, and the solder reflow etc., and the resin of high performance has come to be needed further. The photosensitive polyimide resin with which the technology which gives photosensitivity to polyimide resin itself attracts attention recently, for example, is shown in the following formula (6) on the other hand is mentioned.

[0003]

[Formula 9]



[0004] When this is used, a part of pattern creation process can be simplified, there is an effect of process compaction and the improvement in the yield, but since solvents, such as a N-methyl-2-

pyrrolidone, are needed in the case of development, a problem is in safety and handling nature.

[0005] Then, the photopolymer of the positive type which can do development in an alkali aqueous solution is developed recently. For example, the positive type photopolymer which consists of a poly benzo oxazole precursor and a diazo quinone compound in JP,1-46862,B is indicated. This has high thermal resistance, the outstanding electrical property, and micro-processing nature, and has not only the object for wafer coats but the possibility as resin for layer insulation. Although the diazo quinone compound of the unexposed section is insoluble in an alkali aqueous solution, when the development mechanism of the photopolymer of this positive type is exposed, a diazo quinone compound becomes meltable in a lifting and an alkali aqueous solution about a chemical change. The soluble difference of this exposure section and the unexposed section is used, and creation of the paint film pattern of only the unexposed section is attained by carrying out dissolution clearance of the exposure section.

[0006] When using these photopolymers actually, it is the sensitivity of a photopolymer especially to become important. The exposure time becomes it long that it is low sensitivity, and a throughput falls. Then, it is going to raise the sensitivity of a photopolymer and the problem that the thickness needed is not obtained only by only making molecular weight of base resin small, for example since film decrease of the unexposed section becomes large at the time of development, or a pattern configuration collapses arises. Moreover, when such measures are taken, the mechanical property of the hardening film which carried out the dehydration ring closure with heat, and the nonconformity of falling remarkably happen. Since it is such, development of the photopolymer which is high sensitivity is desired strongly, satisfying the above-mentioned property.

[0007] Moreover, when such a photopolymer is used as a surface-protection film of a semiconductor device, adhesion with the closure resin for a package fabricated at an after process on it poses especially a problem. Since these mainly serve as a permanent protective coat as an object for layer insulation and will exist between a circuit element and closure resin, if adhesion is bad, exfoliation will occur in the interface, a semiconductor package carries out a crack, or water advances into the crack and they generate electric [of a semiconductor / poor].

[0008]

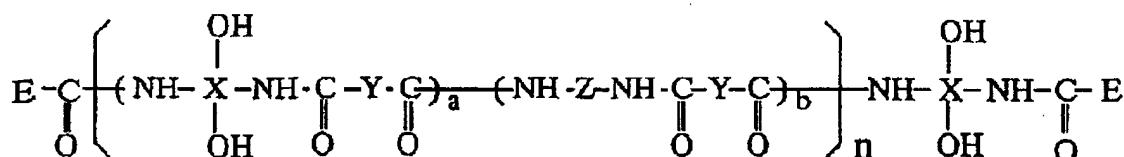
[Problem(s) to be Solved by the Invention] This invention aims at offering the positive type photopolymer which could obtain the pattern of a high remaining rate of membrane by high sensitivity, and was excellent in adhesion with closure resin.

[0009]

[Means for Solving the Problem] this invention -- a general formula -- (-- one --) -- being shown -- having -- a polyamide -- (-- A --) -- 100 -- weight -- the section -- photosensitivity -- diazo one -- a quinone -- a compound -- (-- B --) -- one - 100 -- weight -- the section -- a general formula -- (-- two --) - - expressing -- having -- a phenolic compound -- (-- C --) -- one - 30 -- weight -- the section -- from -- becoming -- things -- the feature -- ** -- carrying out -- a positive type -- a photopolymer -- a constituent -- it is .

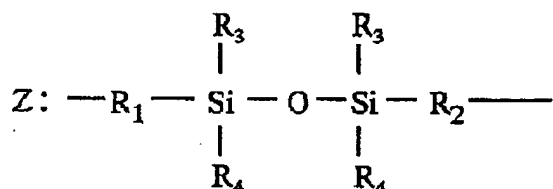
[0010]

[Formula 10]



式中X:4価の環式化合物基
Y:2価の環式化合物基

(1)



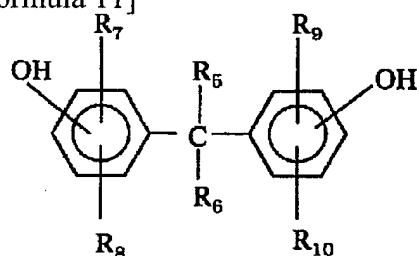
(R_1, R_2 :2価の有機基、 R_3, R_4 :1価の有機基)

E:アルケニル基又はアルキニル基を少なくとも1個を有する
脂肪族又は環式化合物基

a、b はモル分率を示し、 $a+b=100$ モル%
 $a=60.0 \sim 100.0$ モル%
 $b=0 \sim 40.0$ モル%
 $n=2 \sim 500$

[0011]

[Formula 11]



(2)

(式中、 R_5, R_6 は水素原子またはアルキル基を表し、

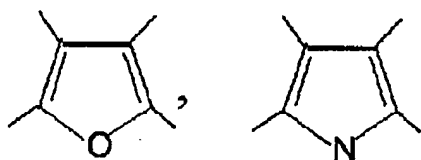
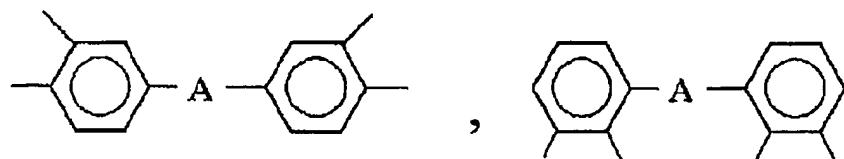
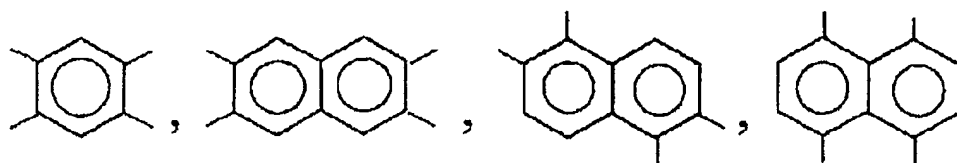
R_7, R_8, R_9, R_{10} はそれぞれ水素原子、ハロゲン原子、水酸基、

アルキル基、アルコキシ基、シクロアルキル基の中から選ばれ

た1つを示す)

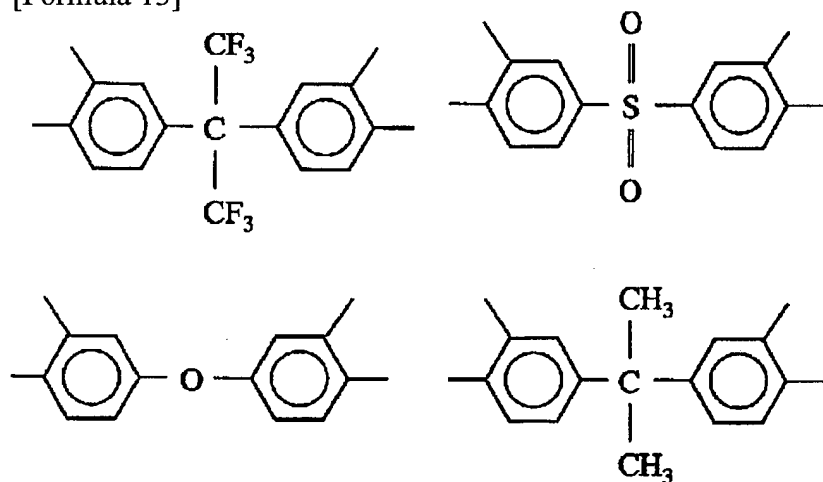
[0012] The polyamide of a formula (1) serves as a bis-aminophenol which has the structure of X, and dicarboxylic acid which has the structure of Y from the acid anhydride which has the structure of E further, if this polyamide is heated at about 300-400 degrees C, a dehydration ring closure will be carried out, and it changes to heat resistant resin called the poly benzo oxazole. X of the polyamide (1) of this invention -- for example [0013]

[Formula 12]

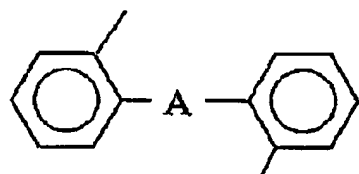
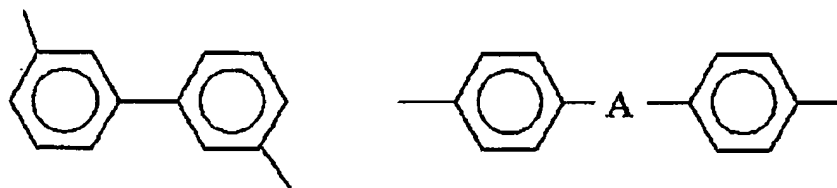
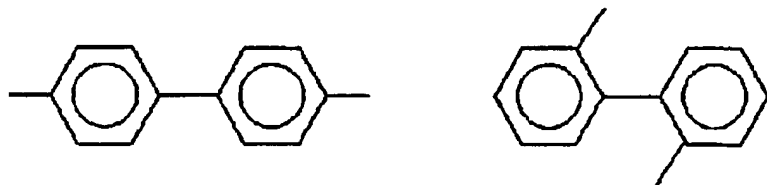
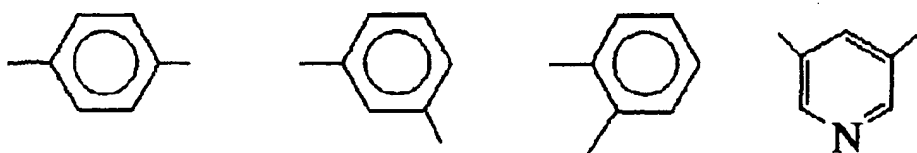


(式中A: $-\text{CH}_2-$, $-\text{C}(\text{CH}_3)_2-$, $-\text{O}-$, $-\text{S}-$, $-\text{SO}_2-$, $-\text{CO}-$,
 $-\text{NHCO}-$, $-\text{C}(\text{CF}_3)_2-$)

[0014] ***** -- although -- it is not limited to these. As a thing especially desirable in these, [0015]
 [Formula 13]

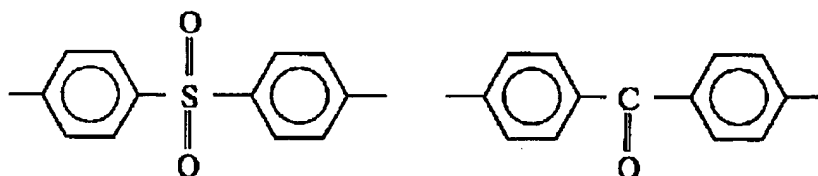
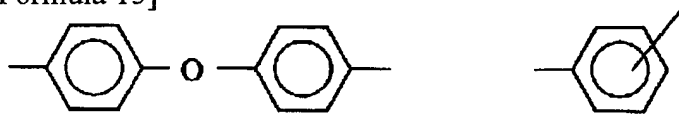


[0016] It is chosen more. Y of ***** (1) -- for example [0017]
 [Formula 14]

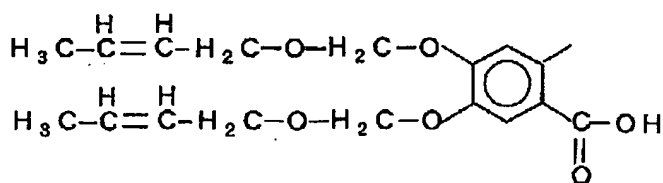
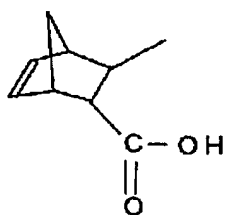
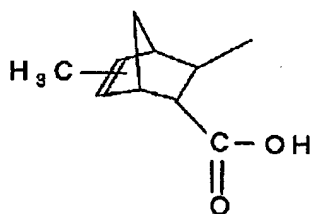
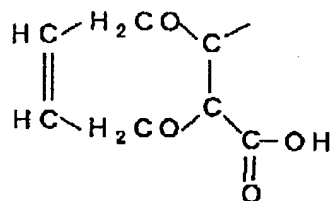
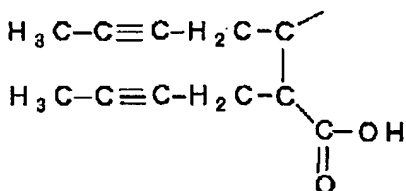
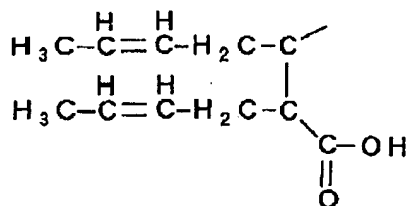
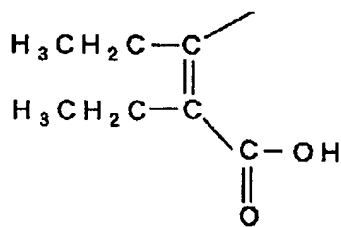
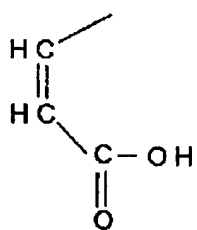


(式中A: $-\text{CH}_2-$, $-\text{C}(\text{CH}_3)_2-$, $-\text{O}-$, $-\text{S}-$, $-\text{SO}_2-$, $-\text{CO}-$,
 $-\text{NHCO}-$, $-\text{C}(\text{CF}_3)_2-$)

[0018] ***** -- although -- it is not limited to these. As a thing especially desirable in these, [0019]
 [Formula 15]



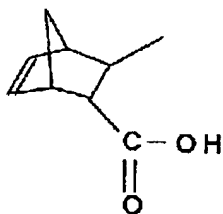
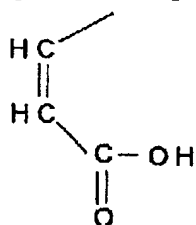
[0020] It is chosen more. E of **** (1) -- for example [0021]
 [Formula 16]



[0022] Although ** is mentioned, it is not limited to these. As a thing especially desirable in these,

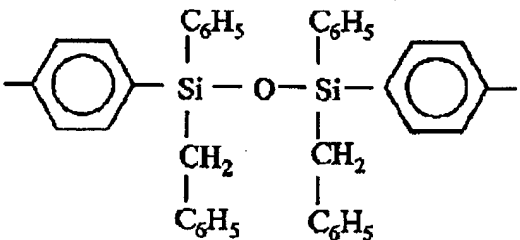
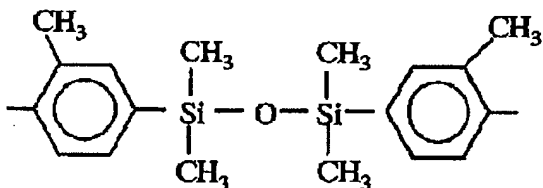
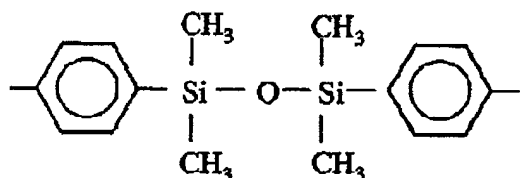
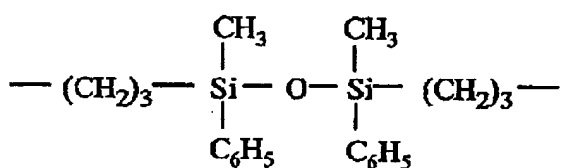
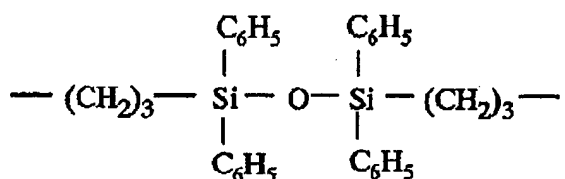
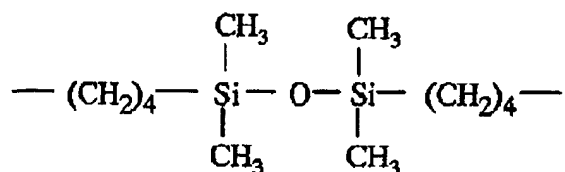
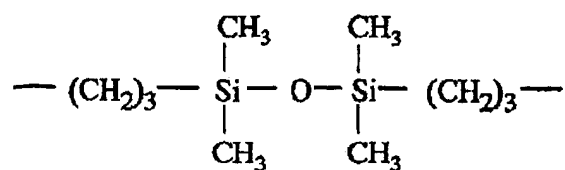
[0023]

[Formula 17]



[0024] It is chosen more. After this invention makes the dicarboxylic acid derivative which has the structure of Y, and the bis-aminophenol which has the structure of X react and compounds a polyamide, it caps the amino group of an end using the acid anhydride which has the alkenyl radical or at least one alkynyl group shown in E of a formula (1). furthermore, Z of a formula (1) -- for example [0025]

[Formula 18]



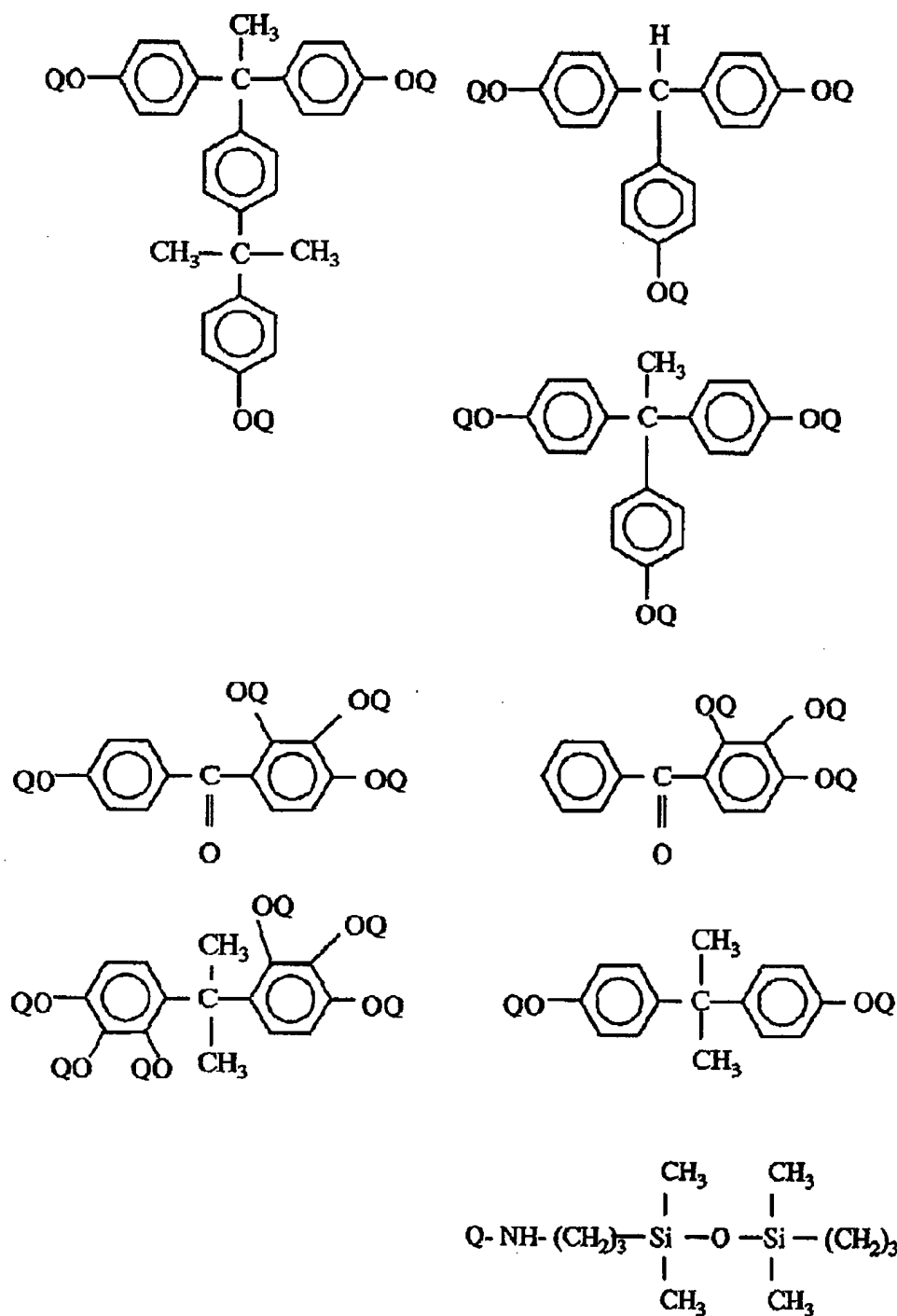
[0026] ***** -- although -- it is not limited to these. Although especially Z of a formula (1) is used to a substrate like a silicon wafer when the outstanding adhesion is required, the operating rate b is to a maximum of 40.0-mol %. If 40.0-mol % is exceeded, the solubility of resin will fall extremely, the remainder (Society for Cutting Up Men) of resin occurs at the pattern pars basilaris ossis occipitalis after development, and pattern processing cannot be performed. In addition, in an activity of these X, Y, E, and Z, it does not matter even if it is one kind, respectively and is two or more kinds of mixture.

[0027] In the positive type photopolymer of this invention, when aiming at high sensitivity, the polyamide component of a formula (1) is the mixture of the polyamide component weight average molecular weight 5000-17000 and whose molecular weight distribution searched for by Mw/Mn are 1-2, and the polyamide component which are weight average molecular weight 30000-70000 and molecular weight distributions 2-4, and it is required to contain the whole for the low molecular weight constituent 20 to 70% of the weight among the amount of whole. The polyamide from which such molecular weight differs can be easily obtained by changing the preparation mole ratio of the bis-aminophenol at the time of compounding, and a dicarboxylic acid derivative. It is difficult to compound with a weight average molecular weight of 5000 or less polymer, and when with a weight average molecular weight of 70000 or more polymer is used, Society for Cutting Up Men generates and is not desirable [a thing] about this polyamide, after development. When the effect of high sensitivity becomes small when a low molecular weight constituent is less than 20% of the weight of the amount of the whole polyamide component, and 70 % of the weight is exceeded, since a pattern configuration not only gets worse, but the amount of film decreases at the time of the development of the unexposed section increases and the mechanical property of the film after making it heat-harden falls, it is not desirable.

[0028] The photosensitive diazo quinone compound used by this invention is a compound which has 1 and 2-benzoquinone diazido or 1, and 2-naphthoquinonediazide structure, and are U.S. Pat. No. 2,772,972, No. 2,797,213, and the matter well-known No. 3,669,658. For example, although the following are mentioned, it is not limited to these.

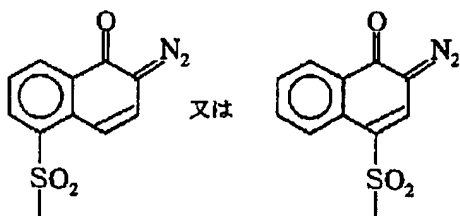
[0029]

[Formula 19]

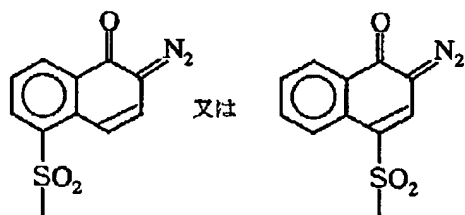


[0030]
[Formula 20]

(式中Qは水素原子又は



を意味し、Qの少なくとも1つは、

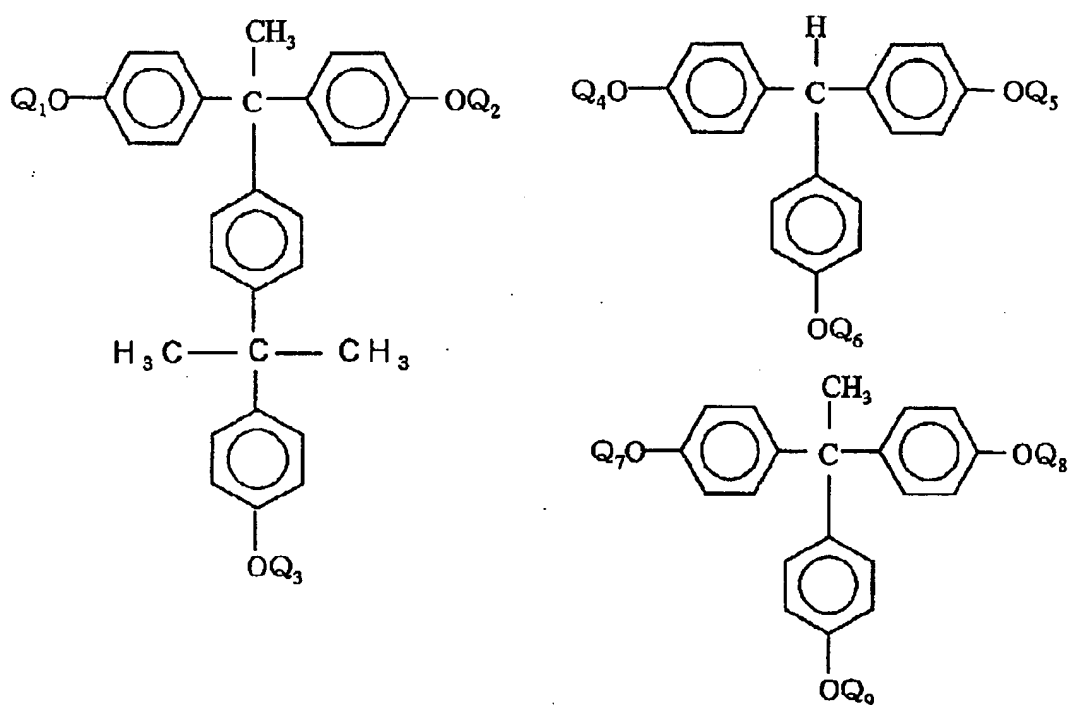


を意味する。)

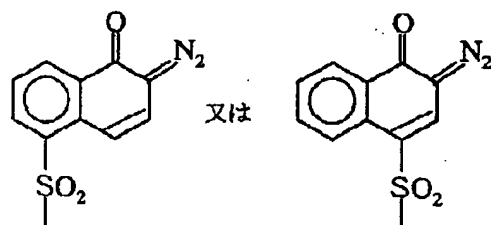
[0031] As a desirable thing, the following are especially mentioned from the point of high sensitivity and a high remaining rate of membrane in these.

[0032]

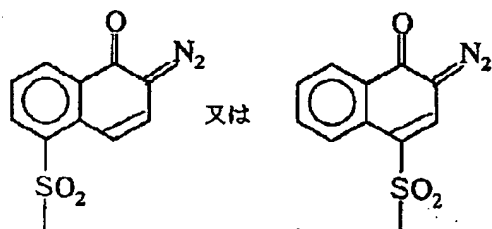
[Formula 21]



(式中 Q_1 、 Q_2 、 Q_3 、 Q_4 、 Q_5 、 Q_6 、 Q_7 、 Q_8 、 Q_9 は水素原子又は



を意味し、 Q_1 、 Q_2 、 Q_3 、 Q_4 、 Q_5 、 Q_6 、 Q_7 、 Q_8 、 Q_9 の少なくとも1つは、



を意味する。)

[0033] The loadings to the polyamide (A) of a photosensitive diazo quinone compound (B) are the 1 - 100 weight section to the polyamide 100 weight section. If loadings are under 1 weight section, the patterning nature of resin will become poor, and if the 100 weight sections are exceeded conversely, not only sensitivity falls substantially, but the hauling pace of expansion of adhesion with closure resin or a film will fall remarkably.

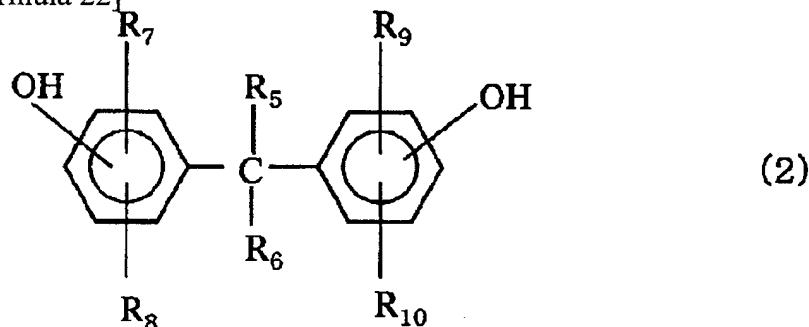
[0034] In order to raise a sensitization property as occasion demands, a dihydropyridine derivative can be added to the positive type photopolymer constituent of this invention. As a dihydropyridine derivative, for example 2, the 6-dimethyl -3, 5-diacetyl-4-(2'-nitrophenyl)-1, a 4-dihydropyridine, 4-(2'-

nitrophenyl)-2, the 6-dimethyl -3, 5-JIKARUBO ethoxy -1, a 4-dihydropyridine, 4-(2' and 4'-dinitrophenyl)-2, the 6-dimethyl -3, 5-JIKARUBO methoxy -1, a 4-dihydropyridine, etc. can be mentioned.

[0035] It is important to make the phenolic compound further shown by the general formula (2) in the positive type photopolymer constituent of this invention contain.

[0036]

[Formula 22]



(式中、 R_5 、 R_6 は水素原子またはアルキル基を表し、

R_7 、 R_8 、 R_9 、 R_{10} はそれぞれ水素原子、ハロゲン原子、水酸基、

アルキル基、アルコキシ基、シクロアルキル基の内から選ばれ

た1つを示す)

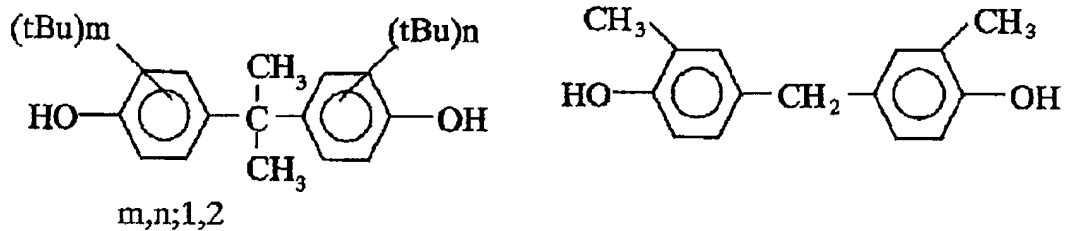
[0037] As technology which adds phenolic compounds to a positive-resist constituent, it is shown in JP,3-200251,A, JP,3-200252,A, JP,3-200253,A, JP,3-200254,A, JP,4-1650,A, JP,4-11260,A, JP,4-12356,A, and JP,4-12357,A, for example. However, even if a phenolic compound as shown in these uses the polyamide in this invention for the positive type photopolymer used as base resin, the effect of the improvement in sensitivity is small.

[0038] However, when the phenolic compound expressed with the general formula (2) in this invention is used, the dissolution rate in the exposure section increases and sensitivity improves. Moreover, film decrease of the unexposed section which is seen when molecular weight of base resin is only made small and sensitivity is raised is also dramatically small. Moreover, in this invention, it found out that the positive type photopolymer constituent whose adhesion with closure resin improved is obtained as a new property by adding the phenolic compound expressed with a general formula (2).

[0039] Although the following can be mentioned as a phenolic compound shown in a general formula (2), it is not limited to these.

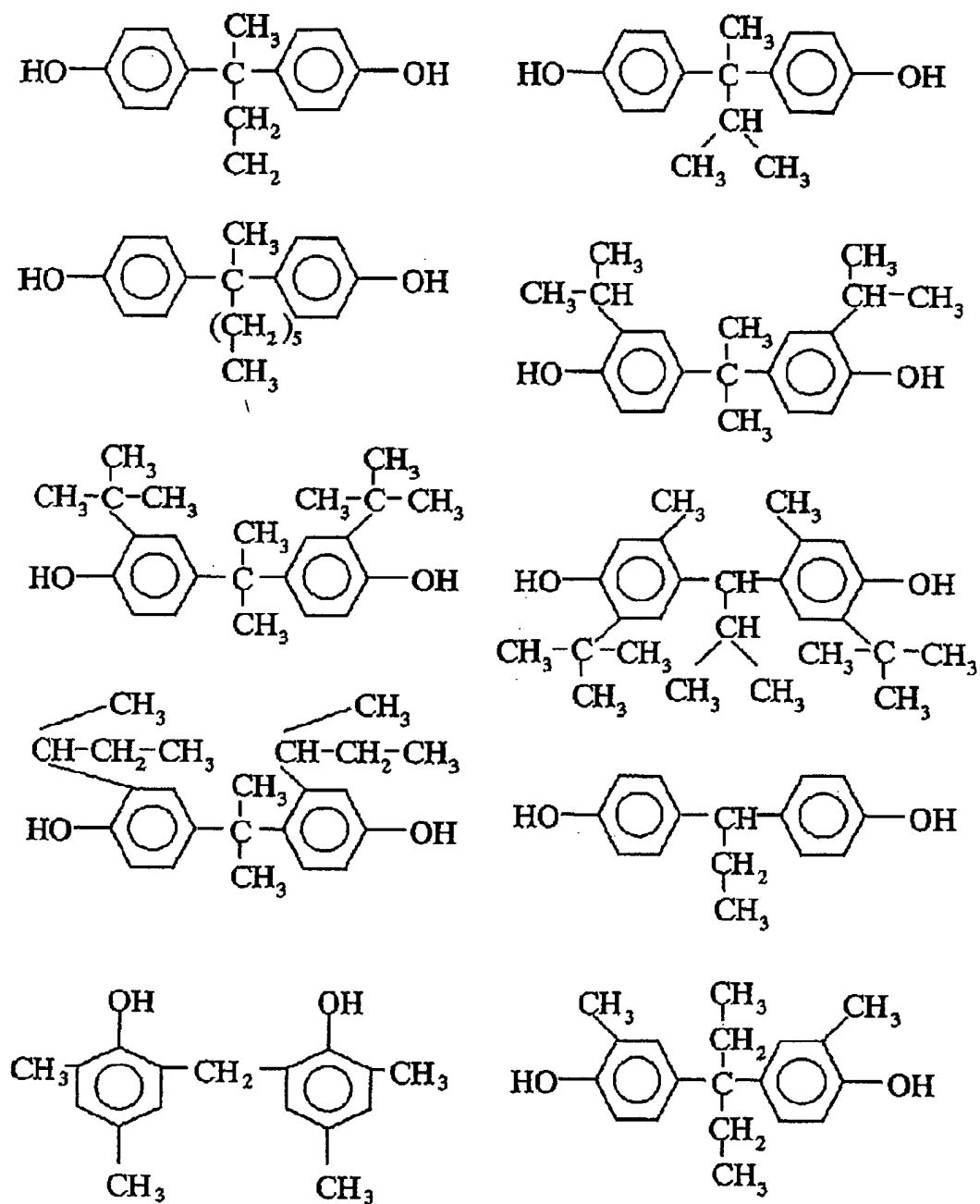
[0040]

[Formula 23]



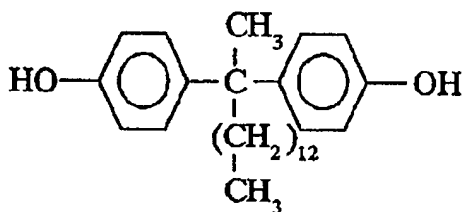
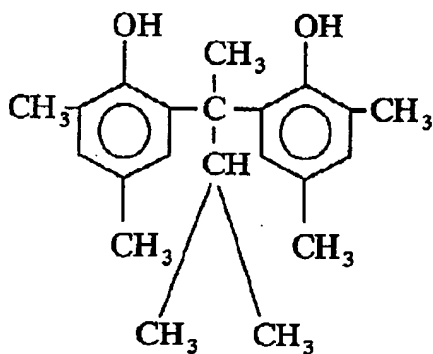
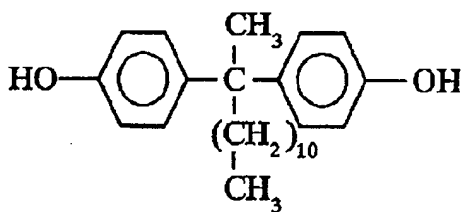
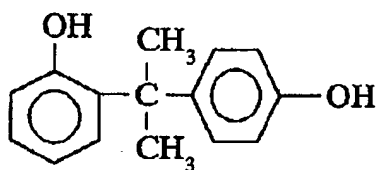
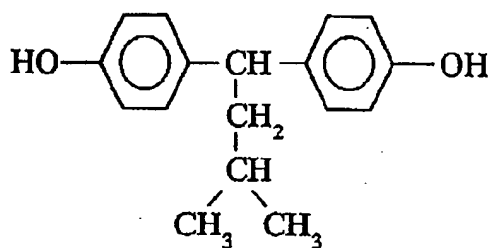
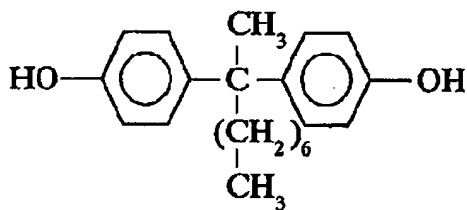
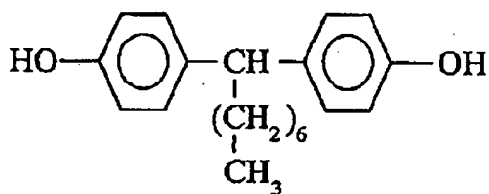
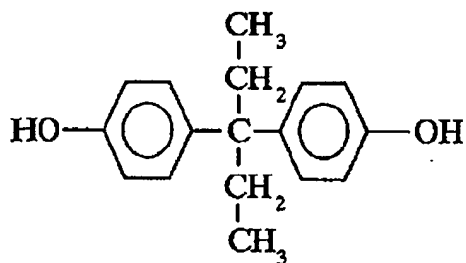
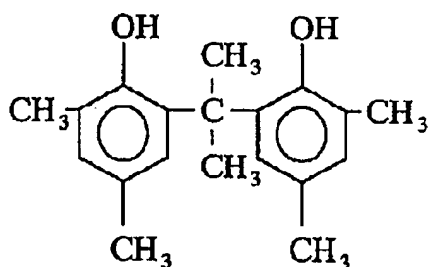
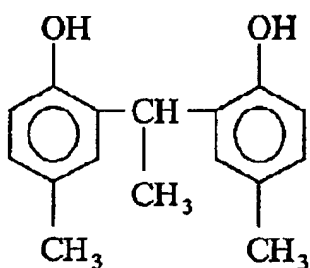
[0041]

[Formula 24]

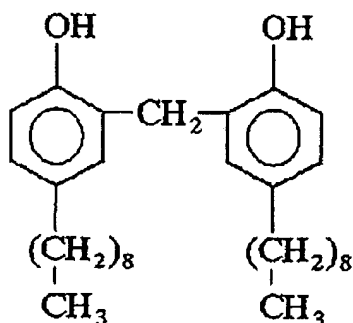
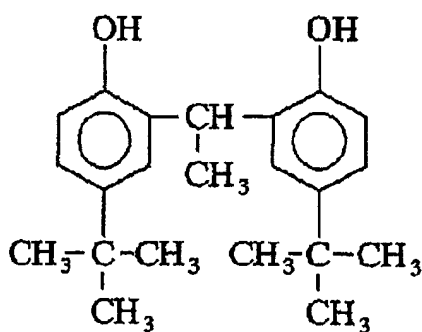
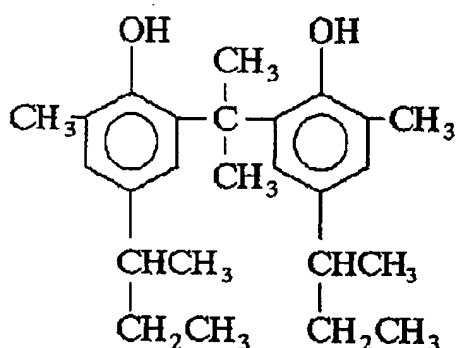


[0042]

[Formula 25]

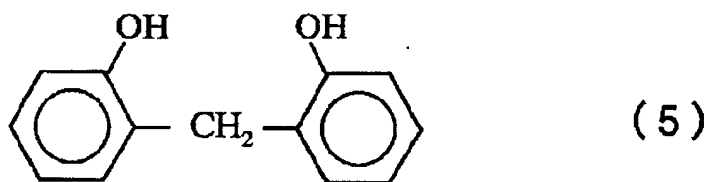
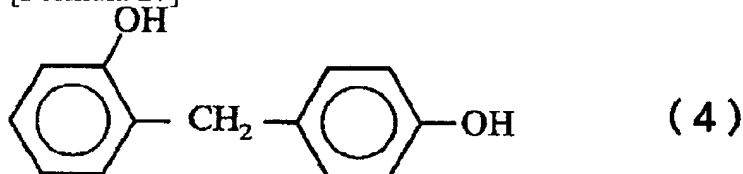


[0043]
[Formula 26]



[0044] In these, it is a desirable thing especially in respect of sensitivity and a remaining rate of membrane, [0045]

[Formula 27]



[0046] It comes out, and it is and the compound expressed with a general formula (4) or (5) is contained 50% of the weight or more in [all] a phenolic compound (C) in the form of independence or mixture. The addition of a phenolic compound (C) has desirable 1 - 30 weight section to the polyamide 100 weight section shown by the general formula (1). When there are more additions of a phenolic compound than 30 weight sections, the remarkable decline in a remaining rate of membrane takes place at the time of development, or a deposit takes place during frozen conservation and practicability is missing. The effect of that adhesion with closure resin falls [an addition] under in 1 weight section or the improvement in sensitivity is not acquired.

[0047] In the positive type photopolymer constituent in this invention, additives, such as a leveling agent and a silane coupling agent, can be added as occasion demands. In this invention, these components are dissolved in a solvent, and it is used by making it the shape of a varnish. As a solvent, a N-methyl-2-

pyrrolidone, gamma-butyrolactone, N,N-dimethylacetamide, dimethyl sulfoxide, diethylene-glycol wood ether, Diethylene-glycol diethylether, diethylene-glycol dibutyl ether, Propylene glycol monomethyl ether, dipropylene glycol monomethyl ether, Propylene-glycol-monomethyl-ether acetate, methyl lactate, Ethyl lactate, butyl lactate, methyl -1, 3-butylene-glycol acetate, 1, the 3-butylene-glycol-3-monomethyl ether, methyl pyruvate, pyruvic-acid ethyl, methyl-3-methoxy propionate, etc. are mentioned, and it may be independent, or you may mix and use.

[0048] The operation of the positive type photopolymer constituent of this invention applies this constituent to a suitable base material, for example, a silicon wafer, a ceramic substrate, an aluminum substrate, etc. first. In the case of a semiconductor device, coverage is applied so that the last thickness after hardening may be set to 0.1-20 micrometers. It becomes difficult to fully demonstrate the function as a protection membrane surface of a semiconductor device as thickness is 0.1 micrometers or less and it not only becomes difficult to obtain a detailed processing pattern as it is 20 micrometers or more, but processing takes time amount and a throughput falls. There are revolution spreading using the spinner as the method of application, fuel-spray spreading using a spray coater, immersion, printing, roll coating, etc.

[0049] Next, it prebakes at 60-130 degrees C, and chemical rays are irradiated after drying a paint film at a desired pattern configuration. As chemical rays, although an X-ray, an electron ray, ultraviolet rays, a visible ray, etc. can be used, a thing with a wavelength of 200-500nm is desirable. Next, a relief pattern is obtained by carrying out dissolution clearance of the exposure section with a developer. As a developer, a sodium hydroxide, a potassium hydroxide, a sodium carbonate, Inorganic alkali, such as a sodium silicate, a meta-sodium silicate, and aqueous ammonia Primary amine, such as ethylamine and n propylamine, diethylamine, The 3rd amines, such as the 2nd amines, such as G n propylamine, triethylamine, and methyl diethylamine, Alcoholic amines, such as dimethylethanolamine and triethanolamine, The aqueous solution of alkali, such as quarternary ammonium salt, such as tetramethylammonium hydroxide and tetraethylammonium hydroxide, And the aqueous solution which carried out suitable amount addition of the water-soluble organic solvents and surfactants like a methanol and ethanol, such as alcohols, can be suitably used for this. As the development method, methods, such as a spray, a paddle, immersion, and an ultrasonic wave, are possible.

[0050] Next, the rinse of the relief pattern formed by development is carried out. Distilled water is used as a rinse. Next, it heat-treats, an oxazole ring is formed and the last pattern which is rich in thermal resistance is obtained. The positive type photopolymer constituent by this invention is useful also as the layer insulation of not only a semiconductor use but a multilayer circuit, the cover coat of a flexible copper-clad sheet, a solder resist film, a liquid crystal orientation film, etc.

[0051]

[Example] Hereafter, an example explains this invention concretely.

<<example 1>>

* The synthetic diphenyl ether -4, one mol of 4'-dicarboxylic acid, 1-hydroxy of a polyamide - 1, 2, two mols of 3-benzotriazols 372.4g (0.93 mols) of dicarboxylic acid derivatives, hexafluoro which were made to react and were obtained - 2 and 2-screw (3-amino-4-hydroxyphenyl) propane 366.3g (1.0 mols) is put into the separable flask of a thermometer, an agitator, raw material input port, and 4 openings equipped with the desiccation nitrogen gas installation pipe, and 3000g of N-methyl-2-pyrrolidones was added, and it was made to dissolve. It was made to react at 75 degrees C for 12 hours using an oil bath after that.

[0052] Next, the 5-norbornene -2 and 32.8g (0.2 mols) of 3-dicarboxylic acid anhydrides dissolved in 500g of N-methyl-2-pyrrolidones were added, it stirred for further 12 hours, and the reaction was ended. After carrying out the ** collection of the charge and the precipitate to the solution of water / methanol =3/1 and washing the reaction mixture after filtering a reaction mixture enough with water, it dried under the vacuum and the target polyamide (A-1) was obtained. The weight average molecular weight of A-1 was 40200, and molecular weight distribution were 2.30. It is diphenyl ether -4, one mol of 4'-dicarboxylic acid, and 1-hydroxy shortly. - The charge of the dicarboxylic acid derivative which two mols of 1, 2, and 3-benzotriazols were made to react, and was obtained was set to 328.4g (0.82 mols), it

compounded similarly, and the polyamide (A-2) of weight average molecular weight 10600 and molecular weight distribution 1.40 was obtained.

[0053] * After dissolving 25g (Q-1) of photosensitive diazo quinone compounds which have the structure of 55g and the following type for polyamide (A-1) 45g in which the positive type photopolymer constituent carried out production composition, and a polyamide (A-2), and 15g (P-1) of phenolic compounds which have the structure of the following type in 200g of N-methyl-2-pyrrolidones, it filtered with the 0.2-micrometer Teflon filter, and the photopolymer constituent was obtained.

[0054] * After using the spin coater and applying the positive type photopolymer constituent of ***** on a silicon wafer, it was dried at 120 degrees C with the hot plate for 4 minutes, and the paint film of about 3 micrometers of thickness was obtained. g line stepper exposure machine NSR-1505 G3A (NIKON CORP. make) increased 10 mJ/cm every 2 from 50 mJ/cm² through reticle to this paint film, and it exposed to 540 mJ/cm². Next, after carrying out dissolution clearance of the exposure section by being immersed in 1.40% of tetramethylammonium hydroxide aqueous solution for 60 seconds, the rinse was carried out for 30 seconds with pure water. Consequently, the pattern is fabricated from the portion irradiated by light exposure 180 mJ/cm², and it has checked that there was no Society for Cutting Up Men in a pattern pars basilaris ossis occipitalis (sensitivity is 180 mJ/cm²). The remaining rate of membrane at this time (thickness x100 before the thickness/development after development) showed 92.0% and a very high value.

[0055] Moreover, it is a positive type photopolymer constituent independently. After having applied on the silicon wafer of two sheets similarly, prebaking and stiffening heating and resin in order (30 minutes in oven / 150 degrees C, 30 minutes / 250 degrees C, and 30 minutes / 350 degrees C), one sheet fabricated the epoxy resin constituent for semiconductor closure (the Sumitomo Bakelite Co., Ltd. make, EME-6300H) on this hardening film in magnitude of 2x2x2mm (horizontal x length x height). As a result of measuring the shear strength of the epoxy resin constituent for closure fabricated on the poly benzo oxazole resin hardening film using tensilon, 3.6kg /was [mm] 2. The one remaining sheets performed dicing so that it might become 10mm width of face, by being immersed in a hydrogen fluoride aqueous solution 2%, washed with water the film which exfoliated from the silicon wafer enough, and dried. When tensile strength was measured for this film by tensilon, the high value 10.5kg /2 was acquired mm.

[0056] <<example 2>> Hexafluoro in an example 1 - 2 and 2-screw (3-amino-4-hydroxyphenyl) propane 366.3g (1.0 mols) was changed to the 3 and 3'-diamino -4 and 4'-dihydroxy diphenylsulfone 280.3g (1.0 mols), and the polyamide which is shown by the general formula (1) and which X becomes by the following formula X-2, and Y becomes from a= 100 and b= 0 by the following formula Y-1 was compounded. The weight average molecular weight of the polyamide (A-3) obtained when the dicarboxylic acid derivative in an example 1 was 0.93 mols was 39000, molecular weight distribution were 2.25, the weight average molecular weight of the polyamide (A-4) similarly obtained at the time of 0.82 mols was 9300, and molecular weight distribution were 1.32. Furthermore, the addition of each component was changed as shown in a table 1, and also the same assessment as an example 1 was performed.

[0057] <<example 3>> Set to the dicarboxylic acid derivative composition in an example 1. Instead of diphenyl ether -4 and one mol of 4'-dicarboxylic acid, one mol of 4 and 4'-benzophenone dicarboxylic acid Moreover, hexafluoro - 3 and 3'-diamino -4 and 4'-dihydroxy diphenyl ether 232.2g (one mol) is used instead of 2 and 2-screw (3-amino-4-hydroxyphenyl) propane 366.3g (one mol). It was shown by the general formula (1) and the polyamide which X becomes by the following formula X-3, and Y becomes from a= 100 and b= 0 by the following formula Y-2 was compounded. The weight average molecular weight of the polyamide (A-5) obtained when the dicarboxylic acid derivative using 4 and 4'-benzophenone dicarboxylic acid was 0.93 mols was 35000, molecular weight distribution were 2.17, the weight average molecular weight of the polyamide (A-6) similarly obtained at the time of 0.82 mols was 8900, and molecular weight distribution were 1.30. It set A-5 when producing a positive type photopolymer constituent, and weight of A-6 to 50g at a time, respectively. Furthermore, the addition of each component was changed as shown in a table 1, and also the same assessment as an example 1 was

performed.

[0058] <<example 4>> Set to composition of the polyamide in an example 1. Hexafluoro - 2 and 2-screw (3-amino-4-hydroxyphenyl) propane is reduced to 348.0g (0.95 mols). It is 1 and 3-screw (3-aminopropyl) to instead of. - 1, 1, 3, and 3-tetramethyl disiloxane 12.4g (0.05 mols) is added, and it is shown by the general formula (1). The following type Y-1 and Z by the following formula Z-1 [X] [the following type X-1 and Y] The polyamide which consists of a= 95 and b= 5 was compounded. The weight average molecular weight of the polyamide (A-7) obtained when the dicarboxylic acid derivative using diphenyl ether -4 and 4'-dicarboxylic acid was 0.93 mols was 41300, molecular weight distribution were 2.33, the weight average molecular weight of the polyamide (A-8) similarly obtained at the time of 0.82 mols was 12000, and molecular weight distribution were 1.42. A-7 when producing a positive type photopolymer constituent and weight of A-8 were set to 42g and 58g, respectively. Others performed the same assessment as an example 1.

[0059] <<example 5>> The charge of the dicarboxylic acid derivative using the diphenyl ether -4 in an example 1 and 4'-dicarboxylic acid was changed into 380.4g (0.95 mols) and 336.4g (0.84 mols), respectively, it was shown by the general formula (1), and the polyamide which X becomes by the following formula X-1, and Y becomes from a= 100 and b= 0 by the following formula Y-1 was compounded. The weight average molecular weight of the polyamide (A-9) obtained when a dicarboxylic acid derivative was 0.95 mols was 59000, molecular weight distribution were 3.06, the weight average molecular weight of the polyamide (A-10) similarly obtained at the time of 0.84 mols was 15600, and molecular weight distribution were 1.56. A-9 when producing a positive type photopolymer constituent and weight of A-10 were set to 40g and 60g, respectively. Furthermore, the addition of each component was changed as shown in a table 1, and also the same assessment as an example 1 was performed.

[0060] <<example 6>> Changed the diazo quinone compound (Q-1) in an example 1 to the following formula (Q-2), further, the addition of each component was changed, as shown in a table 1, and also the same assessment as an example 1 was performed.

<<example 7>> Changed the phenolic compound (P-1) in an example 1 to the following formula (P-2), further, the addition of each component was changed, as shown in a table 1, and also the same assessment as an example 1 was performed.

<<example 8>> The addition of the phenolic compound (P-1) in an example 1 was changed into 5g, and also the same assessment as an example 1 was performed.

[0061] Example of <<comparison 1>> In the example 1, the preparation molar quantity of the dicarboxylic acid derivative at the time of compounding a polyamide (A-2) was changed into 0.91 mols from 0.82 mols, and the polyamide (A-11) of weight average molecular weight 25000 and molecular weight distribution 1.89 was obtained. Furthermore, the addition of each component was changed as shown in a table 1, and also the same assessment as an example 1 was performed.

Example of <<comparison 2>> In the example 1, the preparation molar quantity of the dicarboxylic acid derivative at the time of compounding a polyamide (A-1) was changed into 0.96 mols from 0.93 mols, and the polyamide (A-12) of weight average molecular weight 79200 and molecular weight distribution 3.42 was obtained. Furthermore, the addition of each component was changed as shown in a table 1, and also the same assessment as an example 1 was performed.

Example of <<comparison 3>> In the example 1, the preparation molar quantity of the dicarboxylic acid derivative at the time of compounding a polyamide (A-1) was changed into 0.90 mols from 0.93 mols, and the polyamide (A-13) of weight average molecular weight 22000 and molecular weight distribution 1.77 was obtained. Furthermore, the addition of each component was changed as shown in a table 1, and also the same assessment as an example 1 was performed.

Example of <<comparison 4>> In the example 2, the amount was set to 95g and 5g for A-3 when preparing a positive type photopolymer constituent, and the weight of A-4, respectively. Furthermore, the addition of each component was changed as shown in a table 1, and also the same assessment as an example 1 was performed.

[0062] Example of <<comparison 5>> In the example 2, the amount was set to 10g and 90g for A-3

when preparing a positive type photopolymer constituent, and the weight of A-4, respectively. Furthermore, the addition of each component was changed as shown in a table 1, and also the same assessment as an example 1 was performed.

Example of <<comparison 6>> In the example 1, the addition of a phenolic compound (P-1) was changed into 0g, and also the same assessment as an example 1 was performed.

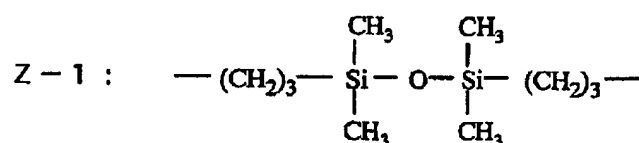
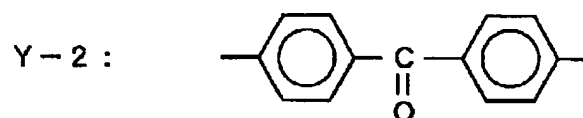
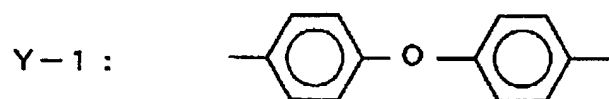
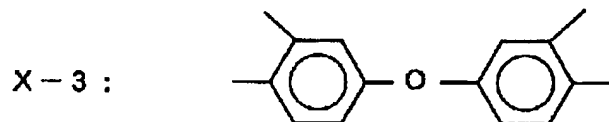
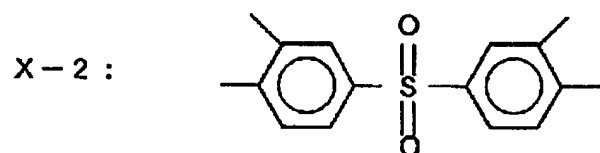
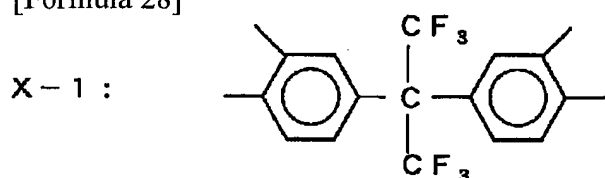
Example of <<comparison 7>> In the example 1, the addition of a phenolic compound (P-1) was changed into 0.5g, and further, the addition of each component was changed, as shown in a table 1, and also the same assessment as an example 1 was performed.

Example of <<comparison 8>> In the example 1, the addition of a phenolic compound (P-1) was changed into 60g, and further, the addition of each component was changed, as shown in a table 1, and also the same assessment as an example 1 was performed.

The assessment result of examples 1-8 and the examples 1-8 of a comparison is shown in a table 2 above.

[0063]

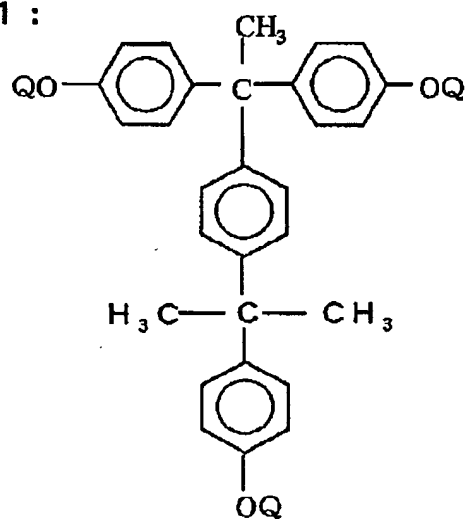
[Formula 28]



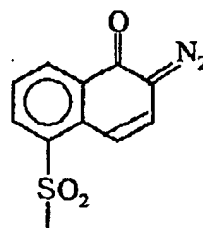
[0064]

[Formula 29]

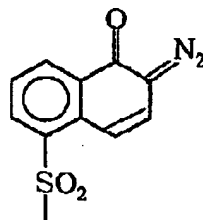
Q-1 :



(式中Qは水素原子又は

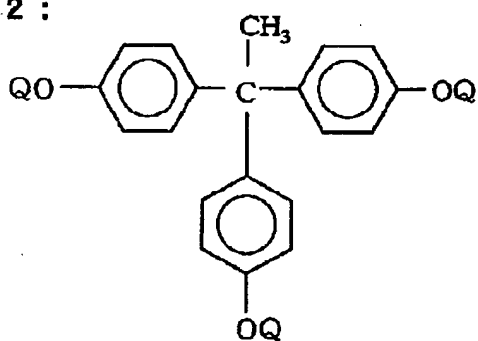


を示し、Q全体の内70%が

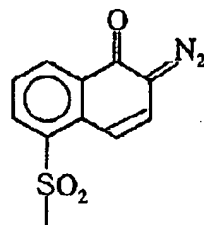


である。)

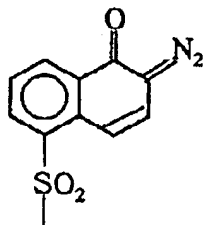
Q-2 :



(式中Qは水素原子又は



を示し、Q全体の内65%が

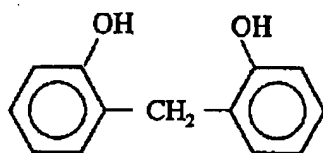


である。)

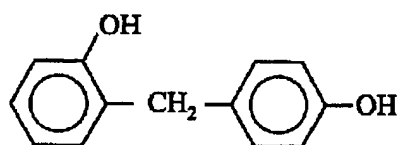
[0065]

[Formula 30]

P-1:



P-2:



[0066]

[A table 1]

表 1

	ポリアミド (A)											ジギキノン 化合物 (B)	フェノール 化合物 (C)
	高分子量成分						低分子量成分						
	アミン	酸	成分	重量平均 分子量	分子量 分布	添加量 (g)	成分	重量平均 分子量	分子量 分布	添加量 (g)			
実施例1	X-1	Y-1	A-1	40200	2.30	45	A-2	10600	1.40	55	Q-1 25	P-1 15	
実施例2	X-2	Y-1	A-3	39000	2.25	45	A-4	9300	1.32	55	Q-1 28	P-1 12	
実施例3	X-3	Y-2	A-5	35000	2.17	50	A-6	8900	1.30	50	Q-1 23	P-1 10	
実施例4	X-1/Z-1 95/5wt%	Y-1	A-7	41300	2.33	42	A-8	12000	1.42	58	Q-1 25	P-1 15	
実施例5	X-1	Y-1	A-9	59000	3.06	40	A-10	15600	1.56	60	Q-1 22	P-1 15	
実施例6	X-1	Y-1	A-1	40200	2.30	45	A-2	10600	1.40	55	Q-2 28	P-1 20	
実施例7	X-1	Y-1	A-1	40200	2.30	45	A-2	10600	1.40	55	Q-1 25	P-2 12	
実施例8	X-1	Y-1	A-1	40200	2.30	45	A-2	10600	1.40	55	Q-1 26	P-1 5	
比較例1	X-1	Y-1	A-1	40200	2.30	45	A-11	25000	1.89	55	Q-1 30	P-1 15	
比較例2	X-1	Y-1	A-12	79200	3.42	45	A-2	10600	1.40	55	Q-1 20	P-1 20	
比較例3	X-1	Y-1	A-13	22000	1.77	45	A-2	10600	1.40	55	Q-1 25	P-1 10	
比較例4	X-2	Y-1	A-3	39000	2.25	95	A-4	9300	1.32	5	Q-1 23	P-1 18	
比較例5	X-2	Y-1	A-3	39000	2.25	10	A-4	9300	1.32	90	Q-1 30	P-1 5	
比較例6	X-1	Y-1	A-1	40200	2.30	45	A-2	10600	1.40	55	Q-1 25	P-1 0	
比較例7	X-1	Y-1	A-1	40200	2.30	40	A-2	10600	1.40	60	Q-1 23	P-1 0.5	
比較例8	X-1	Y-1	A-1	40200	2.30	50	A-2	10600	1.40	50	Q-1 26	P-1 50	

[0067]

[A table 2]

表 2

	感度 (mJ/cm ²)	残膜率 (%)	スラム	引張強度 (kg/mm ²)	せん断強度 (kg/mm ²)
実施例 1	180	92.0	無し	10.5	3.6
実施例 2	170	89.4	無し	9.7	3.3
実施例 3	160	88.0	無し	10.0	3.6
実施例 4	180	92.4	無し	10.1	3.3
実施例 5	170	91.4	無し	10.1	3.4
実施例 6	160	89.1	無し	10.6	3.8
実施例 7	170	90.2	無し	10.3	3.6
実施例 8	200	93.2	無し	10.7	3.0
比較例 1	280	93.4	有り	10.5	3.2
比較例 2	460	95.3	有り	10.7	3.7
比較例 3	170	76.1	無し	8.7	3.3
比較例 4	410	96.3	有り	10.2	3.3
比較例 5	90	60.5	無し	2.4	2.8
比較例 6	270	92.7	無し	10.3	2.4
比較例 7	210	90.3	無し	10.0	2.5
比較例 8	190	66.9	無し	7.3	2.0

[0068]

[Effect of the Invention] The positive type photopolymer which could form the pattern of a high remaining rate of membrane by high sensitivity, and was excellent in adhesion with closure resin with this invention can be obtained.

[Translation done.]